Final Project Report

Exploration of the Fundamental Properties and Consequences of Fluorinated Polyhedral Oligomeric Silsequioxanes (FluoroPOSS)

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Anish Tuteja (tuteja@mit.edu)
[1]Gareth H. McKinley (gareth@mit.edu)
[2]Robert E. Cohen (recohen@mit.edu)

[1]Hatsopoulous Microfluids Laboratory, Department of Mechanical Engineering
[2]Department of Chemical Engineering

Massachusetts Institute of Technology, Cambridge, MA

HATSOPOULOS MICROFLUIDS LABORATORY

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6. AUTHOR(S)
Gareth H. McKinley
Anish Tuteja
Robert E. Cohen

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Massachusetts Institute of Technology
Department of Mechanical Engineering
77 Massachusetts Avenue, Room 3-250
Cambridge, MA 02139

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14. ABSTRACT
Designing and producing highly oil-resistant or 'superoleophobic' surfaces that robustly resist wetting by oily liquids is a challenge that has eluded both nature and material scientists to date. The focus of the research performed under this award was to develop a systematic understanding of the design constraints and engineering/materials solutions required to develop truly oleophobic surfaces.
Theoretical calculations suggest that creating such superoleophobic surfaces would require a surface energy lower than any known material. In this work we demonstrated that a third factor, re-entrant surface curvature, in conjunction with chemical composition and roughened texture can be used to design surfaces that display extreme resistance to wetting from a number of low surface tension liquids.

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Executive Summary

Pour a drop of water on a lotus leaf and it beads up (as shown in Fig. 1A), then rolls off; this is a familiar demonstration of a 'superhydrophobic' self-cleaning surface. Understanding the complementary roles of *surface energy* and *roughness* on such natural non-wetting surfaces has led to the development of a number of biomimetic superhydrophobic surfaces. However, try the same thing with an oily liquid (for example octane or gasoline) and the drop immediately wets the leaf completely (see inset Fig. 1A). Designing and producing highly oil-resistant or '*superoleophobic'* surfaces that robustly resist wetting by oily liquids is a challenge that has eluded both nature and material scientists to date. The focus of the research performed under this award was to develop a systematic understanding of the design constraints and engineering/materials solutions required to develop truly oleophobic surfaces.

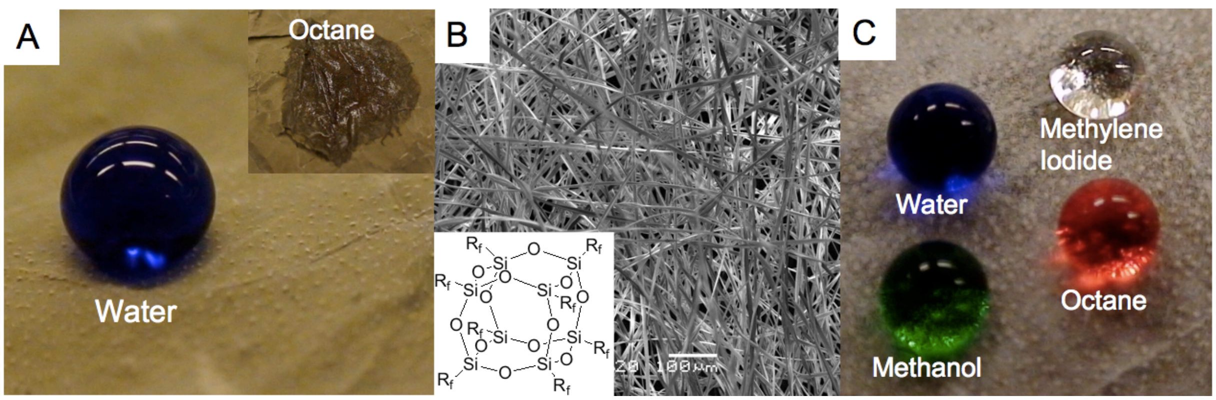

Figure 1. A. A droplet of water on the lotus leaf surface. The inset shows the wetted surface of the lotus leaf after contact with a droplet of octane. **B.** Electrospun fibers of polymethylmethacrylate (PMMA) and fluorodecyl POSS. The inset shows the general molecular structure of fluoroPOSS molecules. The alkyl chains (R_f) have the general molecular formula $–CH_2CH_2(CF_2)_nCF_3$, where n = 0, 3, 5 or 7 (for fluorodecyl POSS, n = 7). C. The electrospun PMMA + fluorodecyl POSS fibers can be deposited even on the fragile lotus leaf to allow it to repel a broad range of liquids, with widely differing surface tensions and chemical characteristics.

Theoretical calculations suggest that creating such superoleophobic surfaces would require a surface energy lower than any known material. In this work we demonstrated that a third factor, *re-entrant surface curvature,* in conjunction with chemical composition and roughened texture, can be used to design surfaces that display extreme resistance to wetting from a number of low surface tension liquids. These non-wetting surfaces are generated by electrospinning fibers (see Fig. 1 B) of PMMA and fluorodecyl POSS particles (developed originally at Edwards Air Force Base, and shown schematically in inset of Fig. 1B). The electrospinning process allows for the possibility of coating surfaces of varying shapes and sizes, and the fibers can even be deposited on the original lotus leaf to make it repellent to a wide range of liquids including water, alcohols and alkanes, as shown in Fig. 1C.

Research Achievements Under this AFOSR Award

1. Development of The First Superoleophobic Surfaces

The combination of surface chemistry and roughness on the micron and nanoscale imparts enhanced repellency to many natural surfaces when in contact with a high surface tension liquid such as water (γ_{lv} = 72.1 mN/m). This understanding had led to a number of biomimetic superhydrophobic surfaces (i.e. apparent contact angles (θ^*) with water greater than 150° and low contact angle hysteresis). However, prior to this work, researchers had been unsuccessful in producing superoleophobic surfaces, which display apparent contact angles θ^* > 150° with liquids having appreciably lower surface tensions such as decane (γ_{lv} = 23.8 mN/m) or octane (γ_{lv} = 21.6 mN/m). Previous calculations suggested that creating such a surface would be impossible as it would require a surface energy lower than any known material. In this work, we demonstrated how a third factor, *re-entrant surface curvature,* could be used to design multiple surfaces that display extreme resistance to wetting and through its synergistic combination with surface chemistry and roughness leads to the first ever truly superoleophobic surfaces (exhibiting low hysteresis and θ^* >160° with both decane and octane; as shown in Fig 1 above).

2. Robust Omniphobic Surfaces

Superhydrophobic surfaces display water contact angles greater than 150° in conjunction with low contact angle hysteresis. Theoretical calculations show that microscopic pockets of air trapped beneath the water droplets placed on these surfaces lead to a composite solid-liquid-air interface in thermodynamic equilibrium. Earlier experimental and theoretical studies had suggested that it may not be possible to form similar fully-equilibrated, composite interfaces with drops of liquids such as alkanes or alcohols that possess significantly lower surface tension than water (γ_{lv} = 72.1 mN/m). In this research we developed surfaces possessing *re-entrant texture* that could support strongly metastable composite solid-liquid-air interfaces even with very low surface tension liquids such as pentane (γ_{lv} = 15.7 mN/m). Furthermore, we outlined four design parameters that predict the measured contact angles for a liquid droplet on a textured surface, as well as the robustness of the composite interface, based on the properties of the solid surface and the contacting liquid. These design parameters allowed us to produce two different families of re-entrant surfaces – randomly-deposited electrospun fiber mats and precisely fabricated micro-hoodoo surfaces – that could each support a robust composite interface with essentially any liquid. These *omniphobic* surfaces display contact angles greater than 150° and low contact angle hysteresis with both polar and non-polar liquids possessing a wide range of surface tensions.

3. Design Guidelines for Superhydrophobic & Superhydrophilic Surfaces

Experimental studies in other research groups (ongoing in parallel with our work) revealed that the wax on the lotus leaf surface by itself is weakly hydrophilic, and conventional understanding would suggest that such a surface should not be able to support a composite interface, leading instead to a fully wetted interface and low contact angles. In this work we reviewed how this unexpected superhydrophobicity is related to the presence of 're-entrant texture' on the surface of the lotus leaf. We then extended this understanding to enable the development of superoleophobic surfaces (i.e. surfaces that repel extremely low surface tension liquids, such as various alkanes), where in most cases no naturally-oleophobic materials exist. We also explored quite general design parameters (denoted H* and T* in Figure 2 below) that allowed us to evaluate the robustness of the composite interface on a particular surface, thereby allowing us to rank in a single unifying "design chart" various superhydrophobic or superoleophobic substrates in the literature, with particular emphasis on surfaces developed from inherently hydrophilic or oleophilic materials.

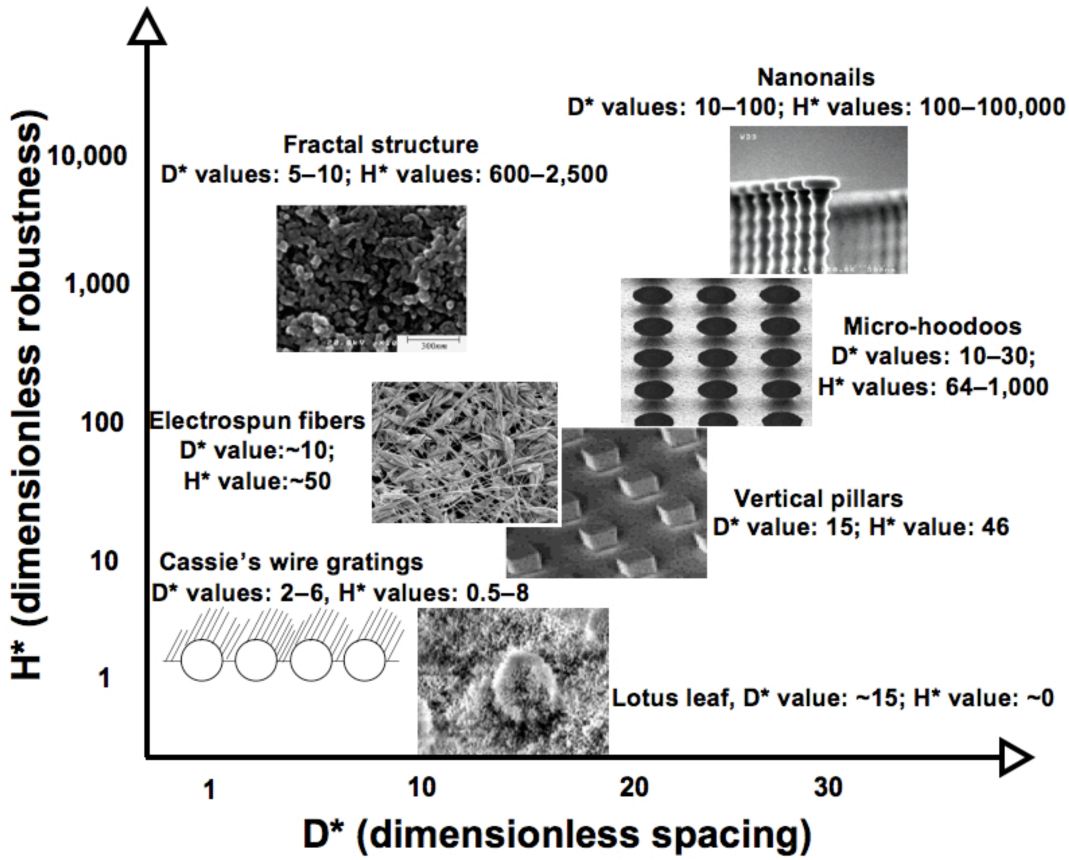

Figure 2. Plot of the robustness parameter (H^*) as a function of the spacing ratio (D^*) for droplets of octane (γ_{lv} = 21.6 mN/m) on various natural and artificial surfaces presented in the literature. More details for each surface, including the values of the apparent contact angles for water and octane, and corresponding design parameters are listed in the original MRS paper. For low surface tension liquids only surface textures for which the D^* and H^* values can be controlled independently (such as micro-hoodoos or nanonails) show both high apparent contact angles and robustness of the composite interface (as evidenced by a high value for H^*) at the same time.

4. Development of Omniphobic Fabrics

The extreme non-wetting behavior demonstrated in our previous work has wide applicability in various fields including the development of self-cleaning surfaces, liquid-liquid separation membranes and anti-fogging films. Various research groups have also tried to develop surfaces that can effectively switch their surface wetting properties in response to changes in their surrounding environment. This includes surfaces that alter their wettability in response to changes in temperature, electrical voltage and mechanical deformation. Because of the difficulty of making surfaces that are strongly repellent to low surface tension liquids such as oils and alcohols, almost all work on switchable wettability had focused on studies with water droplets. In the work outlined above we demonstrated how the incorporation of re-entrant surface texture, (i.e. a multi-valued surface topography) in conjunction with surface chemistry could be used to fabricate superoleophobic surfaces, i.e. surfaces which can support a robust composite (solid-liquid-air) interface and display contact angles greater than 150° with various low surface tension liquids. In this work, we analyzed the consequences of these non-wetting design parameters more extensively. Recognizing the role of re-entrant surface features, we first developed a simple dip-coating process involving fluorodecyl POSS molecules that enabled us to bestow substantially enhanced liquid repellency to any substrate already possessing suitable textures, such as the lotus leaf, commercial fabrics and even duck feathers, by enabling the formation of a composite (solid-liquid-air) interface. Consideration of the geometric scaling of the design parameters then suggested that mechanically deforming a re-entrant structure such as a dip-coated commercial fabric could lead to a dramatic but reversible reduction in the liquid repellency of the surface. Indeed, we observed that a non-wetting drop (initially sitting on the surface in a composite state) was completely imbibed into the fabric texture beyond a critical imposed strain, leading to near zero contact angles. This allowed us to develop, for the first time, surfaces that exhibited reversible, deformation-dependent, tunable wettability, including the capacity to switch their surface wetting properties (between super-repellent and super-wetting) against a wide range of polar and non-polar liquids.

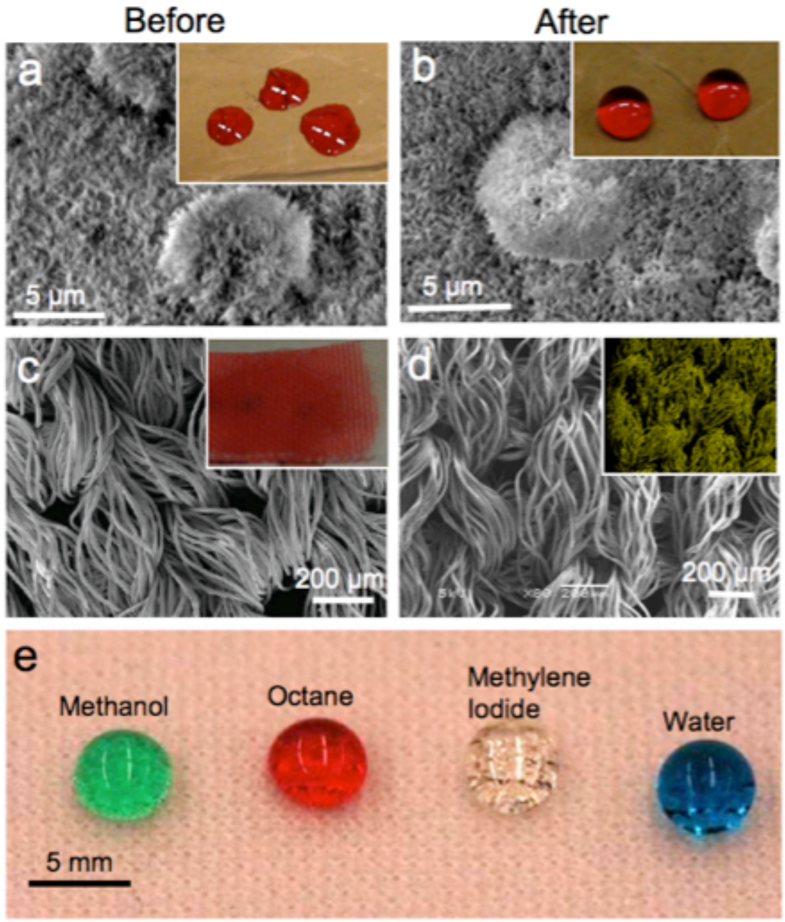

Figure 3. (a) A scanning electron microcope (SEM) image of a lotus leaf illustrating its surface texture. The inset shows that droplets of rapeseed oil easily wet the surface of a lotus leaf. (b) An SEM image of a lotus leaf surface after the dip coating process. (c) An SEM image of the polyester fabric. In spite of the presence of re-entrant curvature, hexadecane can readily wet the fabric surface (inset). (d) An SEM image of the dip-coated polyester fabric. The inset shows the elemental mapping of fluorine obtained using energy dispersive X-ray scattering (EDAXS) (e) Super-repellency of a dip-coated polyester fabric against various polar and non-polar liquids.

4. Understanding Contact Angle Hysteresis on Omniphobic Surfaces

The Cassie-Baxter model is widely used to predict the apparent contact angles obtained on composite (solid-liquid-air) superhydrophobic interfaces. However, the validity of this model has been repeatedly challenged by various research groups because of its inherent inability to provide contact angle hysteresis. In the experimental work discussed above we developed robust omniphobic surfaces that repel a wide range of liquids. An interesting corollary of constructing such surfaces is that it becomes possible to directly image the solid-liquid-air triple phase contact line on a composite interface, using an electron microscope with non-volatile organic liquids or curable polymers. We exploited this capability to fabricate and image a range of model superoleophobic surfaces with controlled surface topography in order to correlate the details of the local texture with the experimentally-observed apparent contact angles. Based on these experiments, in conjunction with numerical simulations, we modified the classical Cassie-Baxter relation to include a local differential texture parameter which enabled us to quantitatively predict the apparent advancing and receding contact angles, as well as contact angle hysteresis. This quantitative prediction also allowed us to provide an *a priori* estimation of roll-off angles for a given textured substrate. Using this understanding we designed model substrates that displayed extremely small or extremely large roll-off angles, as well as surfaces that demonstrated direction-dependent wettability, through a systematic control of surface topography and connectivity.

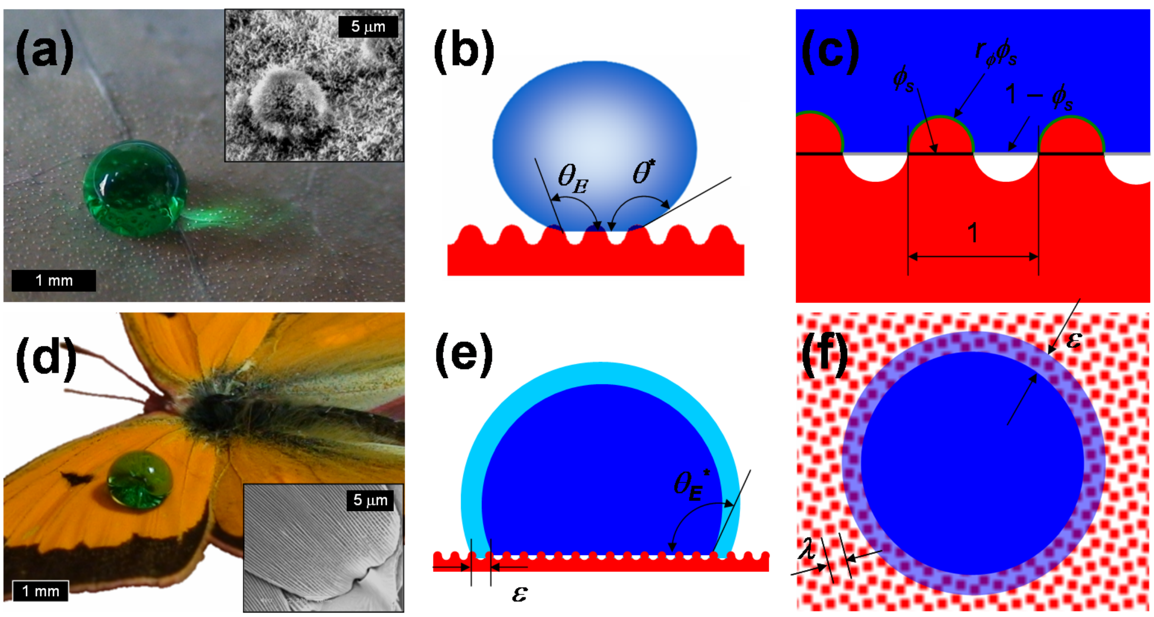

Figure 4. The correlation between the details of the surface texture and the behavior of the contacting liquids. **(a)** A droplet of water (colored green), beading up on a superhydrophobic lotus leaf. The inset shows an SEM image of the lotus leaf, highlighting the multiple scales of roughness present on the leaf's surface. **(b)** A schematic drawing illustrating the formation of a composite interface. **(c)** A schematic illustrating the various characteristic geometrical parameters used in the Cassie-Baxter relation. **(d)** A droplet of water on the wings of a butterfly (*Colias Fieldi*, also known as pinkedged sulphur). The inset shows an SEM micrograph of the wing, and highlights its stripe-shaped surface texture. The water droplet remains pinned on the surface leading to

a significant roll-off angles $\omega > 10°$ when advancing and receding across the striped texture. **(e)** A schematic illustrating the small displacement of the TCL (ε). **(f)** Top view for a droplet as the TCL is displaced from its original position by a distance ε, which is on the same order as the characteristic pitch for a given surface texture (λ).

5. Promoting Slip and Friction Reduction on Omniphobic Surfaces

In this last portion of our AFOSR-funded work, we evaluated the effect of surface topography on the drag-reducing ability of non-wetting textured surfaces, using hydrophobically-modified commercial woven meshes as a simple model substrate. The re-entrant microstructure of the woven mesh, coupled with a strongly hydrophobic fluorinated nanoparticle coating, supports the formation of a robust air film or 'bubble raft' which reduces the total frictional stress generated by a sheared viscous liquid above the mesh. Steady shearing measurements in a rheometer were performed to measure the resulting slip lengths. A parallel-plate configuration allowed us to vary the pressure difference imposed on the air film by systematically changing the gap distance and the shear rate in the fluid. By varying the weave of the mesh, we were able to demonstrate that there is an inherently inverse correlation between the extent of liquid slip (and the corresponding drag reduction) that can be achieved and the robustness of the non-wetting regime to the pressure differentials imposed across the liquid-air portion of the composite interface.

This work is being continued at present by ERC-supported research through Joe Mabry and Tim Haddad.

Staffing & Students

One graduate student and one postdoctoral research associate were supported by this work:

Graduate Student:
Dr. Wonjae Choi (PhD, Mechanical Engineering MIT, August 2009); presently postdoctoral researcher with Prof George Whitesides, Harvard University.

Postdoctoral Researcher
Dr. Anish Tuteja (PhD, Chemical Engineering, Michigan State University, June 2006). Presently Assistant Professor, Michigan University, Dept. of Material Science.

Three undergraduate researchers were also supported in part by AFOSR funds from this project:

Ms. Amalie Revaux (presently graduate student, ESPCI ParisTech)
Mr. Derek Smith (presently graduate student at MIT Dept. Mat Sci & Eng)
Ms. Amy Tsui (presently graduate student, Chemical Engineering, Univ. Rochester)

Publications & Presentations

1. Tuteja, A., Choi, W., Ma, M., Mabry, J.M., Mazzella, S.A., Rutledge, G.C., Cohen, R.E. and McKinley, G.H., Designing Superoleophobic Surfaces, *Science*, **318** (2007), 1618-1622.

2. Tuteja, A., Choi, W., Mabry, J.M., Cohen, R.E. and McKinley, G.H., Robust Omniphobic Surfaces, *Proc. Nat. Acad. Sci.*, **105**(47), (2008), 18200-18205.

3. Tuteja, A., Choi, W., McKinley, G.H., Cohen, R.E. and Rubner, M.F., Design Parameters for Superhydrophobicity and Superoleophobicity, *MRS Bulletin*, **33**(8), (2008), 752-758.

4. Choi, W., Tuteja, A., Chhatre, S., Cohen, R.E. and McKinley, G.H., Fabrics with Tuneable Oleophobicity, *Adv. Mat.*, (2009),**21,** 2190-2196.

5. Choi, W., Tuteja, A., Mabry, J.M., Cohen, R.E. and McKinley, G.H., A Modified Cassie-Baxter Model to Explain Contact Angle Hysteresis and Anisotropic Wettability on Non-Wetting Textured Surfaces, *J. Coll. Int. Sci.*, (2009), **339**(1); 208-216; DOI 10.1016/j.jcis.2009.07.027

6. Choi, W., Chhatre, S.S., Park, K.-C., Cohen, R.E. and McKinley, G.H., Promoting Giant Slip on Omniphobic Surfaces with Cylindrical Textures, *Phys Fluids*, in preparation

AFOSR funds, in conjunction with AFRL funds and ARL support from Natick SSC jointly contributed to two additional papers:

6. S. S. Chhatre, W. Choi, A. Tuteja, J. M. Mabry, G. H. McKinley, R. E. Cohen, Scale dependence of omniphobic mesh surfaces, *Langmuir***, 26(**6), p4027-4035, 2010.

7. S. S. Chhatre, A. Tuteja, W. Choi, A. Revaux, D. Smith, J. M. Mabry, G. H. McKinley, R. E. Cohen, Thermal annealing treatment to achieve switchable and reversible oleophobicity on fabrics, *Langmuir*, **25**(23), p13625-13632, 2009.

Published Conference Proceedings

A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen, Engineering superhydrophobic and superoleophobic surfaces, *NSTI-Nanotech 2008*

A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen, Creating super-oleophobic surfaces, *7th European Coating Symposium 2007, Paris.*

Patents

1. A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen, "Tunable surfaces," International Patent No. WO 2009/009185 A2 Filed 2008; published 2010.

Conference Presentations & Seminars

- The effect of nano/micro surface textures on the behavior of the contacting liquids, Micro/Nano Seminar Series, March 2009, Cambridge MA, USA.
- Exploring contact angle hysteresis and the validity of the Cassie-Baxter equation using super-oleophobic surfaces, 6th International Symposium on Contact Angle, Wettability and Adhesion, July 2008, Orono Maine.
- Effects of surface texture geometry on liquid repellency, MIT-Princeton microsymposium, June 2008, Cambridge MA, USA.
- Superoleophobicity of re-entrant surfaces, Edwards Air-Force Base, March 2008, Edwards CA, USA.
- Constructing robust superoleophobic surfaces using re-entrant surfaces, MRS Fall meeting, November 2007, Boston, MA.
- Re-entrant structures for super-hydrophobic and super-oleophobic surfaces, ACS National meeting, August 2007, Boston, MA.